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Influence of Humic Substances on Photolysis of Nitroaromatic Compounds in Aqueous Systems

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16. ABSTRACT

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INFLUENCE OF HUMIC SUBSTANCES ON PHOTOLYSIS OF NITROAROMATIC COMPOUNDS IN AQUEOUS SYSTEMS

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Abstract—Results are reported for kinetic studies of the photolysis of 19 nitroaromatic compounds in water. The results indicate that dissolved humic substances in natural waters enhance the sunlight-induced photodegradation rates of nitrobenzenes, nitrotoluenes, and nitroxylenes compared to rates observed in distilled water. The largest enhancements, ranging from 2 to 26-fold, were observed for nitroaromatics that are methylated *ortho* to the nitro group. Similar enhancement effects were observed for humic substances obtained from a variety of terrigenous sources, including humus in natural waters and humus extracted from soils.

Key words—nitroaromatics, humic substances, aquatic photochemistry, quantum yields, nitrotoluenes, nitrobenzenes, nitroxylenes, sunlight photolysis

INTRODUCTION

Nitroaromatic compounds are present in a variety of products, including pesticides and explosives. Chemicals in this family have been detected in ambient freshwater and marine environments, drinking water supplies and industrial effluents (Shackelford and Keith, 1976; Hashimoto *et al.*, 1982; Spanggord *et al.*, 1980). Three of the compounds considered in the present study, nitrobenzene, 2,4-dinitrotoluene and 2,6-dinitrotoluene, are listed as priority pollutants in Section 307(a) (1) of the 1977 Clean Water Act. Others are structurally related to important pesticides such as methyl parathion (*O,O*-dimethyl-*O*-*p*-nitrophenyl phosphorothioate) and lampricide (3-trifluoromethyl-4-nitrophenol).

Various laboratory and field investigations have shown that certain nitroaromatic compounds are readily transformed on entry into aquatic environments (Mabey *et al.*, 1983; Callahan *et al.*, 1979). Because nitroaromatic compounds absorb sunlight strongly in the ultraviolet and blue spectral region, they are generally susceptible to photochemical transformation in aquatic systems. For example, field studies by Carey and Fox (1981) of lampricide and by Mabey *et al.* (1983) of trinitrotoluene have shown that photoreactions dominate the behavior of some nitroaromatics in streams and rivers. Other studies also have shown that the environmental photoreactivity of nitroaromatic chemicals varies considerably, being strongly dependent on molecular structure as well as on the natural constituents of aquatic environments (Spanggord *et al.*, 1980; Mabey *et al.*, 1983).

The sometimes-dramatic influence of natural substances on photolysis rates of nitroaromatic compounds is illustrated by studies of Mabey *et al.* (1983). These workers found that the photolysis of trinitrotoluene was accelerated up to 100-fold in natural waters compared to pure water. Zepp and Baughman (1978) and Mabey *et al.* (1983) reported that the enhancement, or "sensitization", of photolysis rates of the nitroaromatics methyl parathion and trinitrotoluene in natural waters is at least in part caused by humic substances in the water. Other studies have shown that humic substances are capable of photosensitizing several types of organic reactions (Mill *et al.*, 1980; Zepp *et al.*, 1985), but little is known about the general susceptibility of nitroaromatics to these humus-induced photoreactions.

The objectives of this study were to first determine how variations in the structure of monocyclic nitroaromatic compounds affect their direct photoreaction rates in distilled water. Then, through studies in sunlight and under artificial light, the influence of various humic substances on photoreactions of these nitroaromatics are determined by comparing results in humus-containing water with those in distilled water. The investigation provides kinetic data, such as reaction quantum yields, and equations that can be used to assess the degradation of nitroaromatic pollutants in a variety of aquatic environments. In addition, information is provided about how natural substances influence the photochemical transformation of chemicals in aquatic systems.

EXPERIMENTAL

Reagents

The water used was doubly distilled; the last distillation was over permanganate solution to obtain organic-free water. The nitroaromatics were purchased from Aldrich

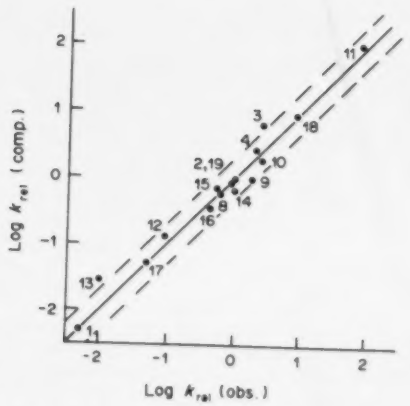

Fig. 1. Comparison of sunlight photolysis rate constants computed using laboratory data (Table 1) and determined from outdoor experiments. Numbers correspond to nitroaromatic compounds listed in Table 1; dashed line indicates factor of 2 from exact agreement (solid line).

of photoproduction of the excited state that reacts, and the reversion of unstable photoproducts back to starting material. Efforts to disentangle the effects of structural changes on these various processes were beyond the scope of this study.

Despite the low quantum efficiencies of the nitroaromatic photoreactions, the photolysis of some of these compounds under full exposure to sunlight is rapid. Computations of average annual rate constants (Table 1) using GCSOLAR program (Zepp and Cline, 1977) indicate that the nitroaromatic compounds substituted by methyl or methoxyl had photolysis half-lives ($0.693/k_a\phi_r$) that are less than 1 day. On the other hand, nitrobenzene and the nitroaromatics with electron withdrawing substituents, because of their lower quantum yields and sunlight absorption rates, photoreact much more slowly (half-lives on the order of weeks to months). The computations in the table are averaged annual values that pertain to near-surface conditions at latitude 40 N. Variations in rate constants caused by changes in season, latitude, and water depth are discussed by Zepp and Cline (1977).

Experiments also were carried out in sunlight at Athens, Ga (latitude 34 N) to determine $k_{rel(observed)}$ [see equation (2)], the sunlight photolysis rate constant ratioed to the rate constant for the *p*-nitroanisole actinometer. These experimental values agreed satisfactorily with theoretical values, $k_{rel(computed)}$, that were calculated using the data in the last column of Table 1 (Fig. 1).

$$k_{rel(computed)} = \frac{k_a\phi_r(P)}{k_a\phi_r(\mathrm{PNA})} \qquad (7)$$

In equation (7), $k_a\phi_r(P)$ corresponds to the nitroaromatic compound and $k_a\phi_r(\mathrm{PNA})$ corresponds to *p*-nitroanisole. Both experiment and theory showed that the value of k_{rel} remained constant with changes in sunlight intensity that result from cloud cover and seasonal changes. The *p*-nitroanisole actinometer and the theoretical basis for its usage are discussed in more detail by Dulin and Mill (1982).

Effects of humic substances on photolysis of nitroaromatic compounds

Natural waters contain various substances that influence the rates of sunlight-induced reactions of pollutants. Past studies have focused mainly on effects of humic substances on photoreactions of pollutants that do not absorb sunlight (Mill *et al.*, 1980; Zepp *et al.*, 1985). Humic substances included in these studies were primarily terrigenous in origin, i.e. the colored organic matter derived from terrestrial plant decay that occurs in soils and in inland and coastal waters. These humic substances have been found to catalyze photoreactions by sensitizing photooxidations and other types of photoreactions. In a detailed study of 2,4,6-trinitrotoluene (TNT), Mabey *et al.* (1983) found that its photolysis was strongly accelerated in certain natural waters and in aqueous solutions of humic substances.

To investigate the generality of the effect of humic substances on photolysis of nitroaromatic compounds, the sunlight photolysis rate constants were determined for a series of nitroaromatics in solutions of humic substances from various sources. Because the earlier work by Mabey *et al.* (1983) had shown no pH effect on photolysis rates of TNT in natural waters, pH effects were not included in the studies. As in the case of the direct photolysis studies discussed above, the *p*-nitroanisole outdoor actinometer was used. The k_{rel} values obtained in these experiments were slightly affected by light attenuation by the humic substances. To estimate near surface values, a correction was applied [equation (4)] assuming that the maximum effect of the sunlight occurs at about 330 nm. This assumption, even if not exact, resulted in only about a 25% correction; the maximum light attenuation correction for these solutions would be only about 30%.

In the first such study, 13 compounds were studied in a water sample from the Aucilla River, a colored river in north Florida, and in solutions of two fulvic acids, one isolated from Wylde Lake in Ontario, Canada, and the other isolated from a soil and sold by Contech ETC. The concentrations of the fulvic acids were adjusted so that the solutions optically matched the Aucilla River water. Zepp and Schlotzhauer (1982) provide a more detailed treatment of the spectral characteristics of humic substances. Results of this study showed that the humic substances enhanced the photolysis rates (compared to distilled water results) of most of the nitroaromatics that were studied.

The enhancements observed in the humus solutions were by far most pronounced in the case of six compounds: *o*-nitrotoluene, 2,6-dinitrotoluene, 2,4-dinitrotoluene, 2-nitro-1,3-xylene, 4-nitro-1,3-xylene

Table 2. Sunlight exposure studies of nitroaromatic compounds in various optically matched solutions containing humic substances*

Compound	k_{rel} (H_2O)	k_{surf} [ratio to k_{rel} (H_2O) is parenthesized]†		
		Aucilla River	Contech fulvic acid	Wylde Lake fulvic acid
Nitrobenzene	0.005	0.007 (1.4)	0.007 (1.4)	—
2,4,6-Trifluoronitrobenzene	0.09	0.13 (1.4)	0.26 (2.9)	0.29 (3.2)
m-Dinitrobenzene	6.01	0.029 (2.9)	0.043 (4.3)	—
o-Nitrotoluene	0.88	6.6 (7.5)	5.6 (6.4)	5.5 (6.2)
m-Nitrotoluene	2.6	3.1 (1.2)	2.7 (1.1)	2.7 (1.1)
p-Nitrotoluene	2.0	2.4 (1.2)	2.4 (1.2)	2.4 (1.2)
2,6-Dinitrotoluene	0.98	17 (17.3)	15 (15.3)	11 (11.0)
2,4-Dinitrotoluene	0.54	2.5 (4.6)	2.5 (4.6)	1.3 (2.4)
2-NO_2-1,3-xylene	0.66	1.3 (2.0)	1.3 (2.0)	0.92 (1.4)
5-NO_2-1,3-xylene	2.5	2.1 (0.9)	2.9 (1.2)	1.9 (0.8)
4-NO_2-1,3-xylene	1.8	4.5 (2.5)	4.3 (2.4)	3.6 (2.0)
4-NO_2-1,2-xylene	83.7	93 (1.1)	92 (1.1)	92 (1.1)
3-NO_2-1,2-xylene	35.4	85 (2.4)	68 (1.9)	40 (1.1)

*Absorbance (1.0 cm pathlength) equalled 0.25 at 330 nm.
†Standard deviations are ≤ 25% of value shown for k_{rel} or k_{surf}.

and 3-nitro-1,2-xylene. All of these compounds have one structural feature in common: a nitro group adjacent, i.e. *ortho*, to a methyl group on the aromatic ring. Compounds with two nitro groups flanking a methyl group—e.g. 2,6-dinitrotoluene and TNT—are particularly susceptible to such catalysis of their photolysis (Mabey *et al.*, 1983). On the other hand, the photolysis rate of the simplest nitroaromatic, nitrobenzene, was hardly affected by the presence of humic substances.

The studies reported in Table 2 also indicated that humic substances isolated from soil or from a natural water body had very similar abilities to catalyze the nitroaromatic photoreactions. To further examine this point, additional studies were conducted with 2,6-dinitrotoluene (Table 3). Results of these studies indicated that the catalytic effects of natural substances in optically matched natural water samples from Georgia and Florida and in an aqueous solution of a riverine fulvic acid isolated from a Georgia river were remarkably similar. In all cases, the rate was enhanced by about one order of magnitude. This similarity strongly indicates that the non-humic organic components of the natural waters used here had no more than a minor effect on the nitroaromatic photochemistry.

Table 3. Effect of various humic substances on photolysis rate of 2,6-dinitrotoluene in water*

Source of humic substances†	TOC‡ (mg l^{-1})	A_{330}§ (cm^{-1})	k_{surf}¶
Aucilla R., Fla	9.6	0.197	9.8
River Styx, Fla	9.6	0.189	12
Okefenokee Swamp, Ga	9.1	0.208	11
Suwannee R., Ga	10.5	0.196	11
Santa Fe R., Fla	9.5	0.183	10
Possum R., Fla	10.0	0.193	14
Fulvic acid isolated from Altamaha R., Ga	13.6	0.212	10
In distilled water			0.98

*Based on exposure to sunlight at Athens, Ga, using *p*-nitroanisole actinometer.
†Except as noted, all experiments conducted in river water samples that were diluted by distilled water.
‡Total organic carbon content of humus solution.
§Absorption coefficient (decadic) of humus solution at 330 nm.
¶First order rate constant ratioed to rate constant for actinometer corrected for light attenuation [equation (4)]; standard deviation ≤ 25% of ratio.

Experiments also were conducted with 2,6-dinitrotoluene to determine the effects of varying the concentration of humic substances on the sunlight photolysis rate constant. Typical results of such experiments are shown in Fig. 2, which pertains to rate studies in water samples from the Aucilla River. The river water was diluted by distilled water to obtain various total organic carbon (TOC) concentrations. The results show that, within experimental error, there is a linear relationship between the photolysis rate constant and TOC.

Prior studies of the behavior of dinitrotoluene isomers in the seawater of Dokai Bay, Japan, indicated that an unidentified environmental process degraded 2,6-dinitrotoluene more rapidly than 2,4-dinitrotoluene (Hashimoto *et al.*, 1982). Based on the results observed in this study, it seems likely that this degradation process is photochemical in nature. As results in Table 2 indicate, the photolysis of the 2,4- and 2,6-isomers of dinitrotoluene is rapid and is enhanced in natural waters. Moreover, consistent with the field observations of Hashimoto *et al.* (1982),

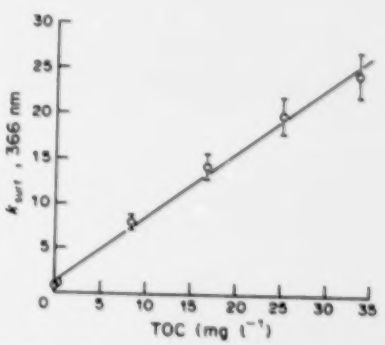

Fig. 2. Photolysis rate constants (366 nm) of 2,6-dinitrotoluene in various dilutions of Aucilla River water.

the 2,6-isomer is more photoreactive than the 2,4-isomer, especially with humic substances present in the water. Humic substances are a likely constituent of the bay water.

CONCLUSIONS

The studies reported here indicate that photolysis rates of nitroaromatic compounds are strongly dependent on the nature of the substituent on the nitroaromatic ring. This variability is mainly attributable to differences in the reaction quantum efficiencies of the compounds. Substitution of the aromatic ring with methyl groups greatly enhances photolysis rates, especially when humic substances are present in the water and the methyl group is *ortho* to the nitro group. The near surface half-lives of all of the methylated nitroaromatic compounds studied were found to be less than one day of average sunlight (latitude 40°N). Direct photolysis rate constants observed for 17 nitroaromatics in outdoor experiments were found to be within a factor of two of those predicted by theory.

Humic substances enhanced the photolysis rates of the nitroaromatic compounds included in this study. The magnitude of the enhancement depended on the ring substituent of the nitroaromatic; compounds with methyl groups ortho to the nitro group were especially susceptible to this effect. Near-surface photolysis rates in the presence of humic substances were directly proportional to the concentration of the humic substance. Humic substances from a variety of terrigenous sources were found to have similar catalytic efficiencies.

The photolysis of dinitrotoluene isomers was found to be rapid in natural waters. The 2,6-isomer photolyzes more rapidly than the 2,4-isomer. This finding is consistent with field studies in Dokai Bay, Japan, which showed that the 2,6-isomer is degraded more rapidly than the 2,4-isomer.

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